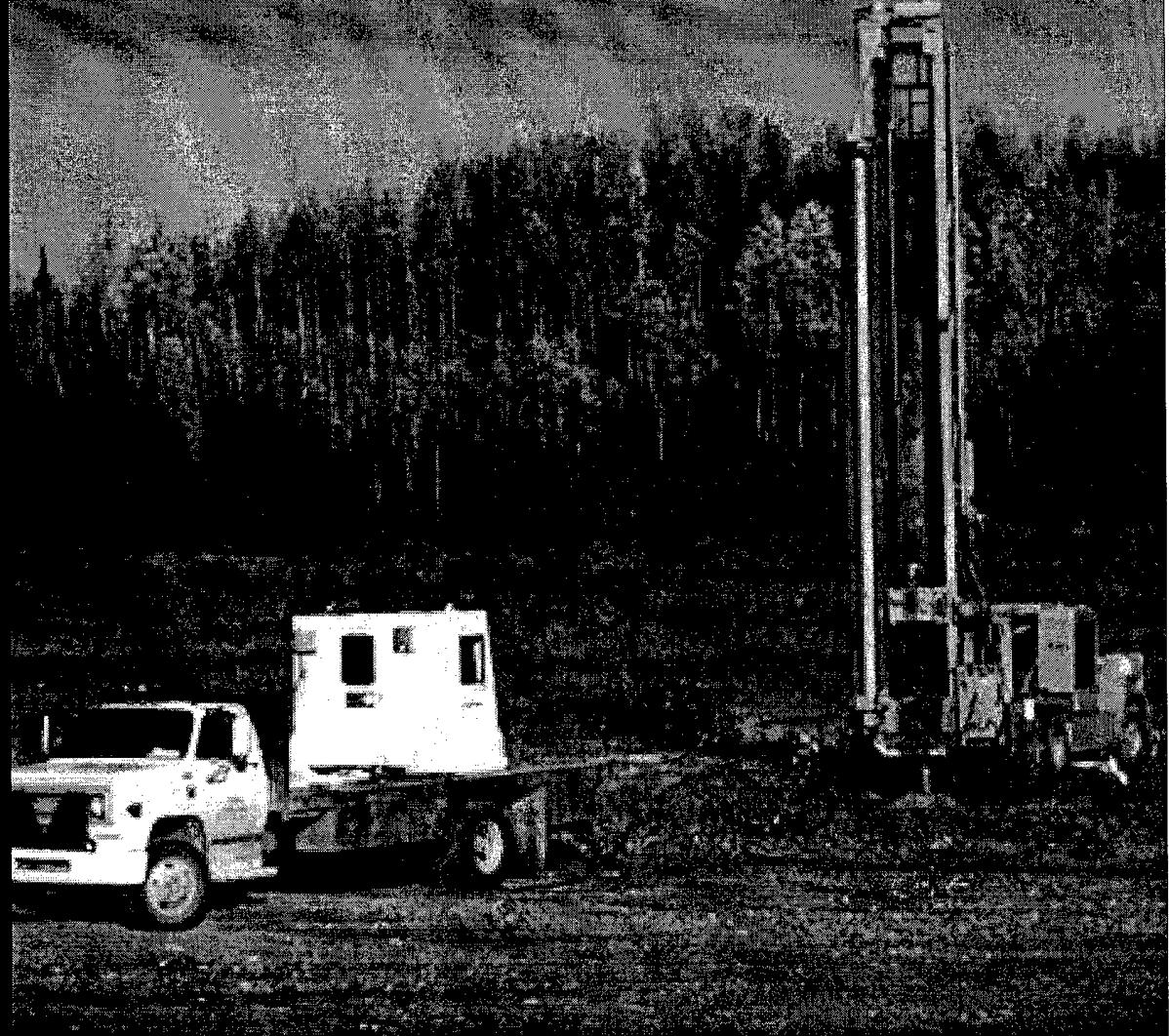# Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using SPE and GC-ECD

Comparison with HPLC

Marianne E. Walsh and Thomas A. Ranney

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Abstract: An analytical method for the determination of nitroaromatic, nitramine, and nitrate ester explosives and co-contaminants in water was developed based on SPE (solid-phase extraction) and GC-ECD (gas chromatograph-electron capture detector). Water samples are pre-concentrated using either cartridge or disk SPE followed by elution with acetonitrile. The acetonitrile extract is compatible with both liquid and gas chromatography, thereby allowing direct comparison of concentration estimates obtained by different methods of determination. Quantitative GC analyses were obtained by using deactivated direct-injection-port liners, short wide-bore capillary columns, and high linear carrier gas velocities. Recoveries from spiked samples were 90% or greater for each of the nitroaromatics and nitrate esters, and greater than 70% for nitramines and amino-nitrotoluenes. Estimates of analyte concentrations in well-water extracts from military sites in the United States and Canada analyzed by GC-ECD and the standard HPLC (high performance liquid chromatography) method showed good agreement for the analytes most frequently detected (HMX [octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine], RDX [hexahydro-1,3,5-trinitro-1,3,5-triazine], TNT [2,4,6-trinitrotoluene], and TNB [1,3,5-trinitrobenzene]). The GC method provides lower method detection limits for most analytes than HPLC, but accurate calibration is more difficult. The ultraviolet (UV) detector used for the HPLC analysis has much greater linear range than the ECD used for GC analysis. In addition, the GC instrumentation requires more care than the LC. Specifically, the injection port liner must be changed frequently to maintain accurate determination of the nitramines. Because the sample preparation technique yields extracts that are compatible with both GC and HPLC analysis, confirmation of analyte presence can be obtained based on different physical properties.

Cover: Drilling a well to monitor groundwater for explosives contamination. The drill is remotely controlled because of the presence of unexploded ordnance.

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MARIANNE E. WALSH AND THOMAS A. RANNEY

INTRODUCTION

Nitroaromatic and nitramine explosives (Table 1) are present in the groundwater at many military installations in the United States (ATSDR 1997) and Europe (Levsen et al. 1993). Potential contamination of drinking water has led to extensive networks of groundwater monitoring wells. Water samples from wells in the United States are generally analyzed by U.S. Environmental Protection Agency SW-846 Method 8330 (USEPA 1994, 1997). This method involves extraction of water samples using either salting-out or solid-phase extraction (SPE) and analysis of the acetonitrile extract using a high-performance liquid chromatograph equipped with an ultraviolet detector (HPLC-UV) (Jenkins et al. 1994). Certified reporting limits (Hubaux and Vos 1970) range from 0.03 to 0.3 µg/L (Jenkins et al. 1994, Winslow et al. 1991), and are sufficiently low for determining whether water quality criteria are met for most of the analytes for which criteria have been determined (Table 2).

Because of the prevalence of gas chromatographs (GC) in environmental labs, an alternative method for explosives based on GC would provide another option for analysis. Some of the Method 8330 analytes are already included as analytes in current gas chromatographic SW-846 methods (USEPA 1997). These include the nitroaromatics NB, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, and the isomers of NT. The physical properties of some of the other Method 8330 analytes, principally the nitramines, would lead one to believe that GC analysis would be impractical. High melting points, low vapor pressures, and thermal lability are characteristic of the nitramines. For example, the melting point of HMX is 275°C (Meyer 1987),

and HMX is reported to decompose prior to boiling. In addition, the vapor pressure of HMX (10^{-14} torr at 20°C [Burrows et al. 1989]) is well below what is typical for GC analytes. Nonetheless, explosives, including the nitramines, have been determined by GC for many years, primarily for forensic applications such as determination of post-blast residues (Yinon and Zitrin 1993). GC methods for the determination of explosives in water are summarized in Table 3. Environmental analysis of explosives has been dominated by HPLC protocols because, for the most part, quantitative GC results have been limited to the nitroaromatics (Levsen et al. 1993).

Hable et al. (1991) were the first to report quantitative GC determination of HMX in water. The nitroaromatics (2,4-DNT, 2,6-DNT, and TNT) were extracted using toluene, and the more polar nitramines (HMX and RDX) were extracted from a separate subsample with glass-distilled iso-amyl acetate. Successful GC analysis was obtained using deactivated injection-port liners, high injection-port temperatures, and short, wide-bore capillary columns. Another factor was the elimination of contact between the analytes and metal parts of the injector. Elution of intact HMX, not a thermal degradation product, from the GC column was confirmed by GC/MS. The certified reporting limits were similar to those obtained using Method 8330 (Jenkins et al. 1992) for RDX, TNT, and 2,4-DNT, significantly higher for HMX, and lower for 2,6-DNT (Table 2).

The goal of our work was to develop a GC method that includes all the Method 8330 analytes in a single extraction step, and that uses commercially available and routinely used instrumentation. We also included other analytes that might be

Table 1. Nitroaromatic, nitramine, and nitrate ester explosives.

Compound	Class	Abbreviation	CAS* number	Vapor pressure ([torr] at ~100°C)	Melting point (°C)	Boiling point (°C)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Nitramine	HMX	2691-41-0	4.3×10^{-9} at 100°C[3]	275[1], 273 & 280[2], 277[3]	
Hexahydro-1,3,5-trinitro-1,3,5-triazine	Nitramine	RDX	121-82-4	1.2×10^{-4} at 97.7°C[3]	204[1,2]	
1,3,5-Trinitrobenzene	Nitroaromatic	TNB	99-35-4	0.375 at 122°C[1]		
1,3-Dinitrobenzene	Nitroaromatic	DNB	99-65-0	0.075 at 90°C[1]		
2,4,6-Trinitrophenylmethylnitramine	Nitroaromatic/ Nitramine	Tetryl	479-45-8	3.5×10^{-5} at 100°C[3]	129.5[1], 130[2], 129.45 pure & 129 technical grade[3]	
Nitrobenzene	Nitroaromatic	NB	98-95-3	20 at 99.3°C[4]	5.7[4]	
2,4,6-Trinitrotoluene	Nitroaromatic	2,4,6-TNT	118-96-7	0.105 at 100°C[1]	81[2], 80–81[3]	345 at atmospheric pressure[3]
4-Amino-2,6-dinitrotoluene	Amino-nitroaromatic	4-Am-DNT	1946-51-0	no data		
2-Amino-4,6-dinitrotoluene	Amino-nitroaromatic	2-Am-DNT	355-72-78-2	no data		
2,4-Dinitrotoluene	Nitroaromatic	2,4-DNT	121-14-2	0.62 at 100°C[1]	70.5[1], 71[2]	300, decomposes[2]
2,6-Dinitrotoluene	Nitroaromatic	2,6-DNT	606-20-2	no data		
2-Nitrotoluene	Nitroaromatic	2-NT	88-72-2	10 at 93.8°C[4]	–4.1[4]	
3-Nitrotoluene	Nitroaromatic	3-NT	99-08-1	10 at 100.5°C[4]	15.5[4]	
4-Nitrotoluene	Nitroaromatic	4-NT	99-99-0	10 at 100.5°C[4]	51.9[4]	
3,5-Dinitroaniline	Amino-nitroaromatic	3,5-DNA	618-87-1	no data		
Nitroglycerine	Nitrate ester	NG	55-63-0	2.3 at 90°C[5]	2.2 labile† & 13.2 stable[2], 13.5 stable & 2.8 labile[3]	145, decomposes[2], 145, decomposes[3], 125 at 2 torr
Pentaerythritoltetranitrate	Nitrate ester	PETN	78-11-5	9.0×10^{-5} at 100°C[3]	141.3[1], 141[2], 141.3[3]	160 at 2 torr[3]

* Chemical Abstract Service Registry Number
† NG labile and stable forms are dipyramidal rhombic crystals and glassy triclinic crystals, respectively.
1–Meyer (1987)
2–U.S. Army Materiel Command (1971)
3–Department of the Army (1984)
4–Perry et al. (1984)
5–Yinon and Zitrin (1993)

Table 2. Certified reporting limits (µg/L) for HPLC methods and water quality criteria.

	Certified reporting limits (µg/L) HPLC					
	Cartridge SPE[1]	Salting-out[2]	Cartridge SPE[2]	Disk SPE[2]	GC[3]	Criteria (µg/L)
HMX	0.30	0.19	0.21	0.33	6	400*
RDX	0.29	0.13	0.27	0.12	0.3	2.0*
TNB	0.45	0.052	0.042	0.051		
DNB	0.15	0.081	0.032	0.036		1.0*
Tetryl	2.49	0.20	0.24	0.83		
TNT		0.086	0.068	0.13	0.06	2.0*
2-Am-DNT	0.16	0.10	0.046	0.055		
2,4-DNT	0.064	0.083	0.085	0.044	0.04	50*, 0.1†
2,6-DNT	0.074				0.003	40*, 0.007†
o-NT	0.41	0.13	0.10	0.20		
p-NT	0.62	0.22	0.12	0.23		
m-NT	1.4	0.21	0.13	0.37		

*EPA Lifetime Health Advisory number
† EPA number for increased cancer risk of 1.0×10^{-6}
1–Winslow et al. 1991
2–Jenkins et al. 1994
3–Hable et al. 1991

Table 3. Summary of GC methods for the determination of explosives in water.

Analytes	Samples	Sample preparation	GC column	Injector	Detector
TNT, 2,4-DNT, Am-DNTs[1]	Groundwater	Solvent extraction with benzene	Packed columns: OV-101 and SP-2250/SP-2401	180°C	ECD
DNTs[2]	Effluent and seawater	Solvent extraction with benzene	20-m SCOT glass coated with Apiezon L grease	180°C	ECD
TNT, DNTs, NTs, Am-DNTs, DNA, other nitroaromatics[3]	TNT wastewater	Solvent extraction with diethyl-ether	60-m SE-30 for FID, packed column for MS	temp not reported	FID,* MS†
TNT, DNT, tetryl, RDX[4]	Drinking water	Solvent extraction with toluene	8.5-m DB-1	190°C	ECD
TNT, DNT, RDX[5]	Groundwater	SPE with XAD-4, ethyl acetate elution	30-m DB-5	40°C on column	ECD
RDX[6]	Groundwater	Evaporation of water, analyte dissolution in acetone	DB-5/30N	not reported	ECD
NB, DNB, NTs, DNTs, other nitroaromatics[7]	Surface water	Compared solvent extraction with dichloromethane to SPE with Amberlite XAD-2, -4, and -8, C18, phenyl, and cyano phases and dichloromethane elution. Solvent exchanged to methanol.	30-m DB-17 and OV-225, DB-5 for MS	not reported	ECD, TEA**, and MS
TNT, DNTs, RDX, HMX[8]	Drinking water	Solvent extraction with toluene and iso-amyl acetate	4.5-m DB-1301, 6-m DB-1	270°C, direct injection and on-column	ECD
TNT, DNTs, NTs, Am-DNTs, Am-NTs, nitrophenols and numerous other analytes[9]	Wastewater, ground-water, surface water	Solvent extraction with toluene or dichloromethane and SPE with C18, ethyl acetate elution	30-m DB-5	on-column and split/splitless, temp not reported	ECD, NPD††, and MS
NB, DNTs[10]	Lake water	Solid-phase microextraction (SPME)	25-m CBP-10	210°C, split/splitless	FID

* Flame-ionization detector
† Mass spectrometer
** Thermal energy analyzer
†† Nitrogen-phosphorus detector

1–Pereira et al. (1979)
2–Hashimoto et al. (1980)
3–Spanggord et al. (1982)
4–Belkin et al. (1985)
5–Richard and Junk (1986)
6–Haas et al. (1990)
7–Feltes et al. (1990)
8–Hable et al. (1991)
9–Levsen et al. (1993)
10–Jang-Yeun Horng and Shang-Da Huang (1994)

present in explosives-contaminated water. We added 3,5-dinitroaniline, the biotransformation product of TNB, and the nitrate esters NG and PETN (Table 1). To complement Method 8330, we sought to use a compatible sample preparation method so that a single extract could be subjected to both GC and HPLC analysis, thereby allowing direct comparisons of concentration estimates obtained by the two methods and providing another method for analyte confirmation.

EXPERIMENTAL METHODS

Calibration standards

Analytical standards were prepared from SARM (standard analytical reference material) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Stock solutions were prepared in acetonitrile. Calibration standards were prepared in acetonitrile over the concentration ranges shown in Table 4. Two sets of standards were prepared because of coelution of

Table 4. Concentration ranges for calibration standards prepared in acetonitrile.

Conc. (µg/L)		Range
0.5 to	500	Set 1: DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, 4-Am-DNT, 2-Am-DNT
2.5 to	500	Set 2: 3,5-DNA, Tetryl
1.0 to	1,000	Set 1: NB, RDX
5 to	5,000	Set 1: o-NT, m-NT, p-NT, HMX
25 to	5,000	Set 2: PETN
50 to	10,000	Set 2: NG

RDX and PETN on the analytical column, as described below. Each set contained 10 standards that were analyzed initially to determine linearity of the gas chromatograph-electron capture detector (GC-ECD). For subsequent analyses, the concentration range was narrowed based on the detector's linear range, and the number of standards analyzed was reduced to a minimum of five standards.

Matrices

Blank matrices used for spike recovery and method detection limit (MDL) studies were reagent-grade (Type 1) water (MilliQ, Millipore)

and groundwater from a domestic well in Weathersfield, Vermont. Field-contaminated samples were obtained from Louisiana Army Ammunition Plant (AAP) (Doyline, Louisiana), Kansas AAP (Parsons, Kansas), Umatilla Army Depot (Hermiston, Oregon), and Canadian Forces Bases (CFB)-Valcartier (Quebec).

Sample preparation

Details of the final procedure are in Appendix B. For each sample, up to 1000 mL of water was preconcentrated using SPE. Both Waters (Milford, Massachusetts) Sep-Pak Vac Porapak RDX cartridges and Empore (St. Paul, Minnesota) SDB-RPS 47-mm disks were used. The Sep-Pak Vac Porapak RDX cartridges were conditioned according to manufacturer's directions, which specify passage of acetonitrile, then reagent-grade water through the solid phase prior to the water sample. For the SDB-RPS disks, Empore recommends rinsing the disks with acetone, isopropanol, methanol, then water. We followed this solvent sequence except that after methanol and before water, we also rinsed with acetonitrile, which thus became the last organic conditioning solvent. After passage of each water sample through the solid phase, air was drawn through the solid phase for 15–20 min to remove as much residual water as possible. The solid phases were eluted with 4 to 5 mL of acetonitrile, and each extract was directly injected into the GC-ECD. When necessary, field sample extracts were diluted with acetonitrile so that peak heights would be bracketed by calibration standards.

Solvents used for conditioning the solid phases were HPLC-grade from Sigma-Aldrich (Milwaukee, Wisconsin) or Baker (Phillipsburg, New Jersey).

Instrumentation

We configured the GC based on the work of Hable et al. (1991). The GC parameters were as follows:

GC: Hewlett Packard (Wilmington, Delaware) HP 5890 with electron capture detector (Ni[63])

Column: Fused silica 100% polydimethylsiloxane, 0.53-mm i.d., 1.5 µm, 6 m (J and W [Folsom, California] DB-1)

Injection-port liner: Restek (Bellefonte, Pennsylvania) Direct Injection Uniliners (deactivated)

Injection-port temperature: 250°C (varied from 200 to 300°C)

Injection volume: 1 µL

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Carrier: Hydrogen (Linear velocity varied from 30 to 185 cm/s.)

Makeup: Nitrogen (38 mL/min)

Oven program: 100°C for 2 min, 10°C per min ramp to 200°C, 20°C per min to 250°C, hold for 5 min.

Detector temperature: 300°C.

Temperature programs for confirmation columns are given in captions later in this paper and in Appendix B.

RESULTS AND DISCUSSION

GC setup

Injection port

The GC injection port is frequently the site of loss of thermally labile analytes (Grob 1994). Deactivation of the liners reduces loss (Levsen et al. 1993), but is a laborious process, involving acid soaking, water rinsing, silanization in an inert atmosphere, and solvent rinsing. In the last few years, deactivated injection-port liners have become commercially available; these have greatly facilitated the analysis of labile analytes.

Trace analysis by GC may be performed by splitless injection or direct injection. Splitless injection is not generally appropriate for reactive or high boiling compounds such as explosives due to adsorption, condensation, and discrimination against high boiling compounds in the injection port. However, splitless injection is required for narrow-bore capillary columns. Wider-bore capillary columns (0.32- and 0.53-mm i.d.) permit direct injection in which all sample and solvent is transferred to the column. The column press-fits into the hourglass-shaped end of the glass inlet liner, eliminating contact with metal parts in the injector. Direct injection liners are commercially available that fit split/splitless ports or packed column injection ports modified to accept wide-bore capillary columns. We chose to use deactivated direct injection Uniliners available from Restek. Uniliners are available for both split/splitless and packed ports.

Selection of analytical column

Initially, we tested a 0.53-mm-i.d. polydimethylsiloxane (DB–1) column at a length (15 m) typically provided by the manufacturer to see if the Method 8330 analytes were resolved. With the exception of HMX, which did not produce a peak, the 8330 analytes eluted as individual peaks in order of decreasing vapor pressure, indicating that this column provides adequate resolution for these analytes. However, the additional analyte

a. Linear velocity = 44 cm/s.

b. Linear velocity = 76 cm/s.
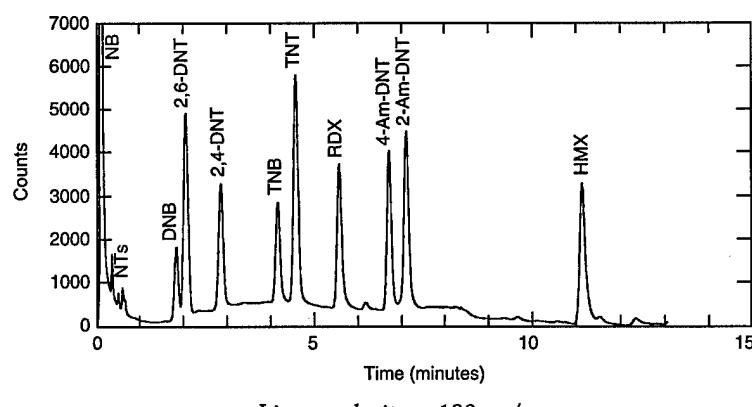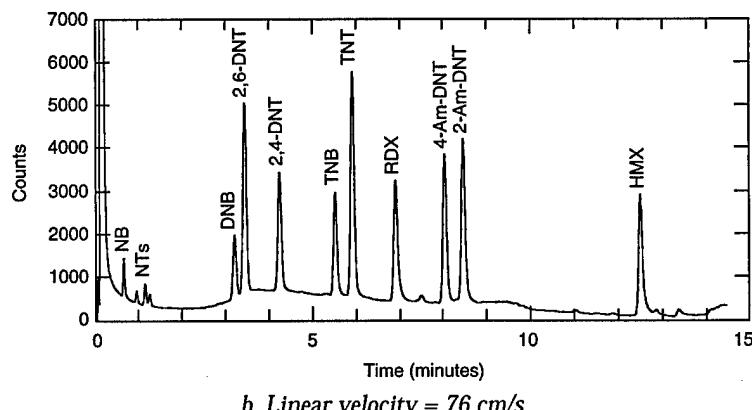

c. Linear velocity = 126 cm/s.
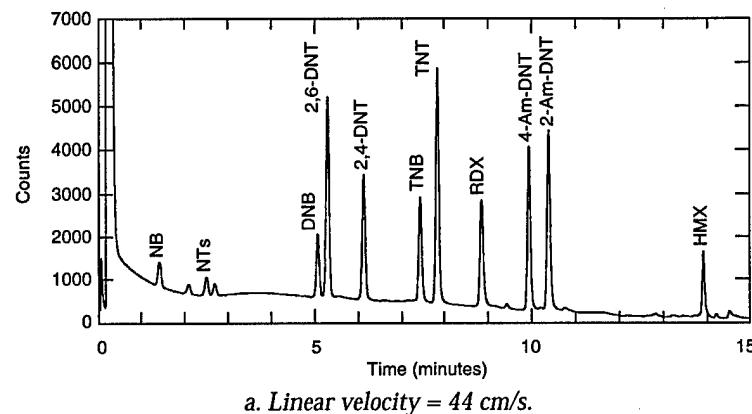
Figure 1. Calibration standard (from set 1 in Table 4) analyzed using DB-1 at three carrier gas velocities. Higher linear velocities resulted in higher HMX peak heights. Linear velocities correspond to those listed in Table 5.

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PETN, which has a vapor pressure almost identical to that of RDX, coeluted with RDX. At explosives-contaminated sites, RDX is by far the more commonly found of these two analytes. Further work with mid-range polarity columns, described below, resolved PETN from RDX, but led to co-elutions with other analytes.

We experimented with different column temperature programs and injected a high-concentration solution of HMX onto the 15-m column. With a high-temperature (250°C) isothermal run, HMX eluted as a broad jagged peak on the 15-m column. We next shortened the GC column to 6 m, as suggested by Hable et al. (1991) and found that HMX now eluted as a sharp peak (Fig. 1). This dramatic improvement was not due to total time in the GC; rather, the decreased column length exposed the analyte to less surface area. Tamiri and Zitrin (1986) reported similar results when they observed that PETN and RDX failed to elute intact from a 30-m column but did elute from a 15-m column. Thus length of a typical GC capillary column is an important consideration for successful chromatographic analysis of the most thermally labile explosives.

We also tested an Alltech (Deerfield, Illinois) MultiCapillary SE-54 (5% phenyl methylpolysiloxane) column. These columns are only 1 m long and are composed of a bundle of over 900 liquid-phase coated 40-μm capillaries. They provide rapid analysis of pesticides, and accommodate high carrier gas velocities, so we reasoned they might be suitable for the analysis of explosives. We tested numerous chromatographic conditions and found that the column was suitable for the analysis of NB, the nitrotoluenes, DNB, and the DNTs. Resolution of the other analytes was poor, the peaks for TNB, TNT, and RDX were uncharacteristically small, and HMX did not elute at all. Here again, large column internal surface area, not total time in the GC, may contribute to HMX loss.

Confirmation columns

We tested four 0.53-mm-i.d. columns for suitability as confirmation columns. In order of increasing polarity, these columns were J and W DB-1301 (6% cyanopropylphenyl methylpolysiloxane), J and W DB-17 (50% phenyl methylpolysiloxane), Restek RTX-200 (Crossbond trifluoropropyl methylpolysiloxane), and Restek RTX-225 (50% cyanopropylmethyl-50% phenyl methylpolysiloxane). The DB-1301 was not acceptable because TNB coeluted with TNT, and DNB co-eluted with 2,6-DNT. The DB-17 was not suitable because TNB coeluted with TNT. The Restek RTX-200 resolved the 8330 analytes at low linear velocity, but HMX is not detected (Fig. 2a). At high linear velocity, HMX was detected (Fig. 2b, Table 5), but PETN coeluted with RDX and 2-Am-DNT, and DNA was not resolved from 4-Am-DNT. Finally, on the RTX-225, tetryl coeluted with RDX, and HMX was not detected (Fig. 2c). However, in subsequent analysis of well-water samples from Louisiana AAP, we found this column to be excellent for confirmation

Table 5. Retention times (minutes) obtained for analytical and confirmation columns using temperature programs given in Figures 1 and 2.

Analyte	DB-1 LV = 126 (cm/s)	DB-1 LV = 76 (cm/s)	DB-1 LV = 44 (cm/s)	RTX-200 LV = 40 (cm/s)	RTX-200 LV = 122 (cm/s)	RTX-225 LV = 108 (cm/s)
NB	0.32	0.63	1.38	2.15		
o-NT	0.47	0.92	2.06	2.78		0.95
m-NT	0.57	1.12	2.47	3.40		1.20
p-NT	0.62	1.22	2.69	3.72		1.40
NG	1.18	2.00	3.84	8.57	0.52	6.25
DNB	1.84	3.18	5.05	9.01	0.63	5.86
2,6-DNT	2.07	3.42	5.28	8.51	0.55	5.50
2,4-DNT	2.88	4.22	6.12	10.64	0.88	6.51
TNB	4.19	5.50	7.42	18.90	1.98	9.99
TNT	4.61	5.91	7.82	17.81	1.86	9.51
PETN	5.62	6.83	8.79	28.52	2.74	11.57
RDX	5.62	6.89	8.83	29.19	2.86	13.66
4-Am-2,6-DNT	6.77	8.02	9.92	23.80	2.45	12.65
3,5-DNA	6.83	8.11	10.07	26.08	2.65	13.32
2-Am-4,6-DNT	7.17	8.45	10.38	28.57	2.85	13.17
Tetryl	8.05	9.34	11.26	32.11	3.54	13.65
HMX	11.21	12.50	13.92	not eluted	6.29	not eluted
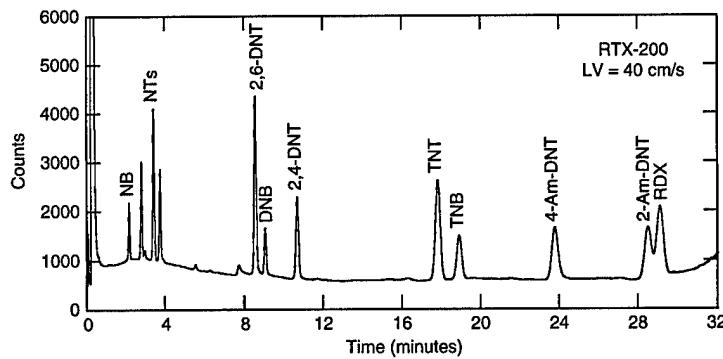
a. Oven 100°C for 1.2 min, 5°C/min to 140°C, 1°C/min to 160°C, 20°C/min to 250°C, hold. Injector 250°C. Detector 290°C.
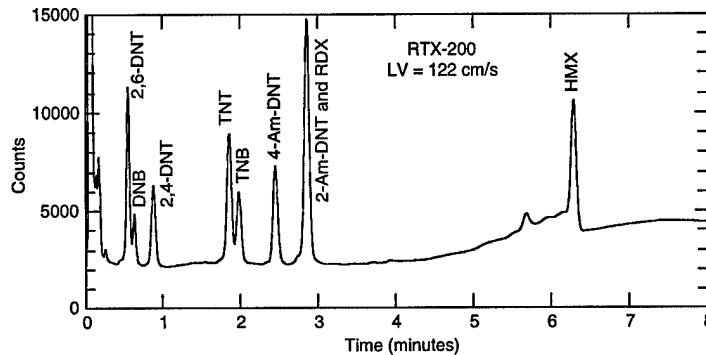
b. Oven 150°C for 1 min, 20°C/min to 250°C, hold. Injector 270°C. Detector 290°C.
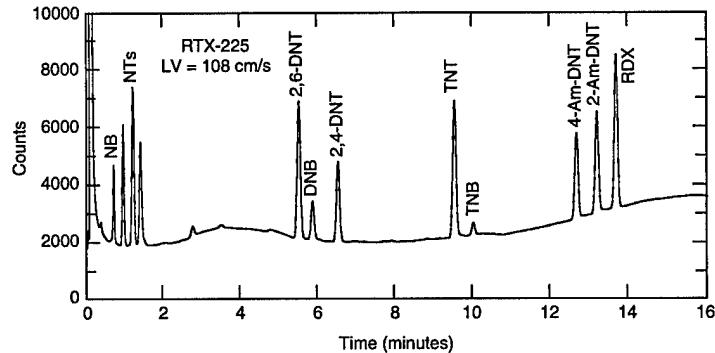
c. Oven 100°C for 2 min, 10°C/min to 220°C, hold for 8 min. Injector 220°C (column maximum). Detector 250°C.

Figure 2. Chromatograms obtained on confirmation columns. DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, 4-Am-DNT, 2-Am-DNT at 50 μg/L, RDX at 100 μg/L, and NB, o-NT, p-NT, m-NT, and HMX at 500 μg/L.

of the amino-DNTs. Thus, for confirmation, extracts must be analyzed under the appropriate conditions. Both the RTX-200 and RTX-225 look promising for confirmation because the elution order of several analytes is the reverse of that on the DB-1. For example, 2,6-DNT and DNB reverse order, as do TNT and TNB. In addition, RDX elutes after the amino-DNTs whereas it elutes before the amino-DNTs on the DB-1 (Table 5).

Effect of carrier gas linear velocity

While testing various temperature programs and carrier gas linear velocities, we noticed that the HMX peak height changed significantly with

changes in linear velocity (Fig. 1). We systematically changed the linear velocity to document this effect.

Van Deemter curves indicate that optimum linear velocity for peak resolution is 26 cm/s when using hydrogen carrier gas and a 0.53-mm-i.d. column. When using direct injections, the manufacturer of the inlet liners recommends using twice the optimum linear velocity to prevent tailing of the solvent front and sharpen early eluting peaks. We tested the effect of increasing carrier gas linear velocity over the range 30 to 185 cm/s and found a significant increase in response from HMX, RDX, NG, and PETN (Fig. 3a, b). For example, no peak was observed for HMX at the lowest linear velocity tested. The linear velocity was increased to 55 cm/s and HMX eluted as a sharp peak. Thereafter, the HMX peak height approximately doubled with each doubling of the linear velocity (Fig. 3). Some degradation in peak resolution did occur. Peak widths of the late eluters increased with increasing carrier gas linear velocity, and the peak for dinitroaniline merged with the peak for 4-amino-DNT. Thus a mid-range carrier gas velocity would be appropriate for most analyses.

The calibration factors for 50-µg/L solutions of all the analytes were determined at three carrier gas velocities (Table 6). The calibration factors for HMX, NG, and PETN were two to three times greater at the highest linear velocity compared with the lowest linear velocity. Also, the response of the ECD varies considerably from analyte to analyte. For the nitrotoluenes, the calibration factor for TNT was more than 10 times greater than those for the mono-nitrotoluenes. This variability in relative response needs to be considered when preparing calibration standards and in setting expectations for detection limits.

Effect of injection-port temperature

Hable et al. (1991) found increased HMX response with increasing injection-port temperature, and recommended an injection-port temperature of 270°C for the determination of TNT, DNTs, RDX, and HMX. High injection-port temperatures were needed to volatilize the nitramines. We reexamined the effect of injection-port temperature at high linear carrier gas velocity (133 cm/s) for the 8330 analytes plus NG, PETN,
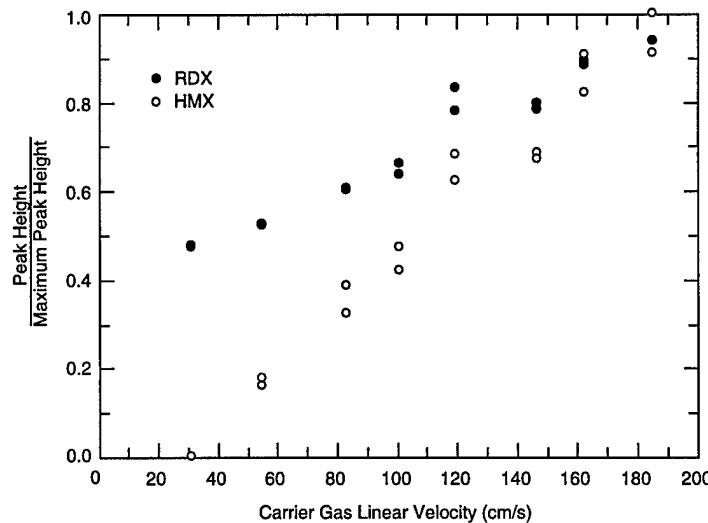
a. RDX and HMX.
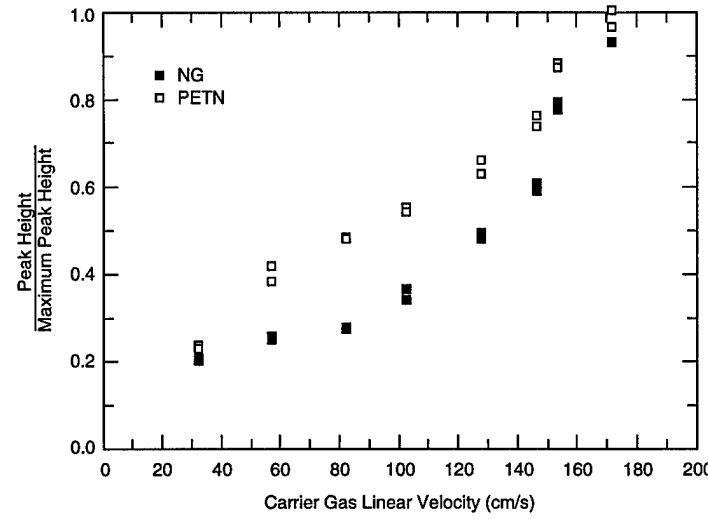
b. NG and PETN.

Figure 3. Effect of carrier gas linear velocity on peak height.

and DNA. We found that maximum GC response was obtained at different temperatures for the different analytes (Table 7). In general, the lowest temperatures tested (200 to 220°C) resulted in the highest response for the nitrotoluenes and nitrate esters. Higher temperatures (250 to 270°C) were best for the HMX, RDX, the amino-DNTs, and DNA. However, the effect of injection-port temperature was minor for most of the analytes. Only HMX, NG, and PETN showed somewhat consistent trends. An injection-port temperature of 250°C would be suitable for most analyses.

Calibration

Traditional ECDs typically have a narrow linear range (approximately fortyfold), with a dynamic range of about a thousandfold (McNair

Table 6. Calibration factors obtained at different carrier gas linear velocities using a DB-1 column and 50-g/L solutions.

Analyte	Calibration factors (peak height/[µg/L])		
	126 cm/s	76 cm/s	44 cm/s
TNT	104	106	109
2,6-DNT	91	90	92
2-Am-DNT	80	77	83
RDX	79	57	52
HMX	75	59	32
4-Am-DNT	71	71	76
DNA	69	65	69
2,4-DNT	58	55	58
Tetryl	46	48	59
TNB	45	48	50
DNB	30	29	28
NB	18	21	9.9
PETN	17	13	8.1
NG	12	4.9	4.5
m-NT	7.5	7.0	7.4
o-NT	5.9	6.6	3.6
p-NT	2.5	5.8	4.5

and Bonelli 1969). This narrow linear range is inconvenient for quantitative analysis of samples that can vary over three orders of magnitude in analyte concentrations. The SW-846 criterion for linearity is that the relative standard deviation (RSD) of the mean calibration factor be less than or equal to 20% for five standards at different concentrations. The calibration data we obtained show linear models relating responses to concentrations that are not appropriate over the entire concentration ranges we tested. SW-846 (USEPA 1997) lists

four options, in order of increasing difficulty, for nonlinear calibration data: adjust the instrument or perform instrument maintenance; narrow the calibration range until response is linear (<20% RSD for calibration factor); use a linear calibration model that does not pass through origin; use a nonlinear calibration model.

From the shapes of the curves of peak height data for TNT, 2-Am-DNT, and RDX over the range 0.5 to 100 µg/L (Fig. 4), which are representative of calibration curves for the other analytes, we see that fitting the data to straight lines, whether through the origin or not, is not at all appropriate. Narrowing the concentration range does bring the average calibration factors for most of the analytes within 20% RSD threshold for linearity prescribed in SW-846. This very limited linear range of the ECD is a disadvantage compared to the HPLC-UV, which has a broad linear range. For GC-ECD, sample extracts would need to be diluted within the proper calibration range. For samples with multiple analytes at varying concentrations, a single extract may require several determinations at different dilution factors. Alternatively, nonlinear models in the form of second-order polynomials fit the data over broader concentration ranges (Fig. 4). Using nonlinear calibration models complicates computations, but reduces the number of reanalyses of multi-analyte samples.

Instability of low-concentration trinitroaromatic standards

The low-concentration calibration standards for

Table 7. Effect of injection-port temperature on GC response when the carrier gas linear velocity was 133 cm/s.

Normalized response*	Temperature (°C)										
	200	210	220	230	240	250	260	270	280	290	300
NB	1	0.95	0.77	0.82	0.76	0.94	0.88	0.87	0.88	0.87	0.84
o-NT	1	0.94	0.79	0.80	0.73	0.88	0.82	0.80	0.81	0.79	0.76
m-NT	1	0.96	0.86	0.85	0.80	0.92	0.86	0.84	0.86	0.83	0.81
p-NT	1	0.96	0.87	0.84	0.79	0.89	0.83	0.82	0.82	0.80	0.78
DNB	0.98	0.98	1.00	0.93	0.93	1.00	0.99	0.95	0.99	0.99	0.87
2,6-DNT	0.95	0.96	1.00	0.95	0.91	0.99	0.98	0.94	0.97	0.98	0.94
2,4-DNT	0.99	0.95	1.00	0.95	0.90	0.98	0.97	0.95	0.97	0.97	0.97
TNB	1	0.98	0.95	0.95	0.89	0.92	0.93	0.94	0.90	0.87	0.86
TNT	1	0.99	0.90	0.98	0.85	0.89	0.92	0.93	0.90	0.83	0.82
RDX	0.95	0.94	1.00	0.95	0.95	1.00	0.97	0.99	1.00	0.96	0.97
4-Am-2,6-DNT	0.92	0.91	0.98	0.93	0.92	0.97	1.00	0.98	0.99	1.00	0.97
2-Am-4,6-DNT	0.92	0.91	0.97	0.94	0.92	0.96	1.00	0.96	0.97	0.99	0.96
HMX	0.71	0.77	0.87	0.83	0.90	0.97	0.95	1.00	1.00	0.96	0.95
NG	0.96	1.00	0.96	0.93	0.92	0.94	0.90	0.85	0.85	0.80	0.82
PETN	0.96	1.00	0.93	0.95	0.93	0.89	0.92	0.92	0.91	0.86	0.87
3,5-DNA	0.89	0.93	0.94	0.94	0.94	0.99	0.97	1.00	1.00	0.98	0.98
Tetryl	0.97	0.98	0.97	0.91	0.96	0.90	1.00	0.90	0.87	0.81	0.88

*([peak height]/[maximum peak height])

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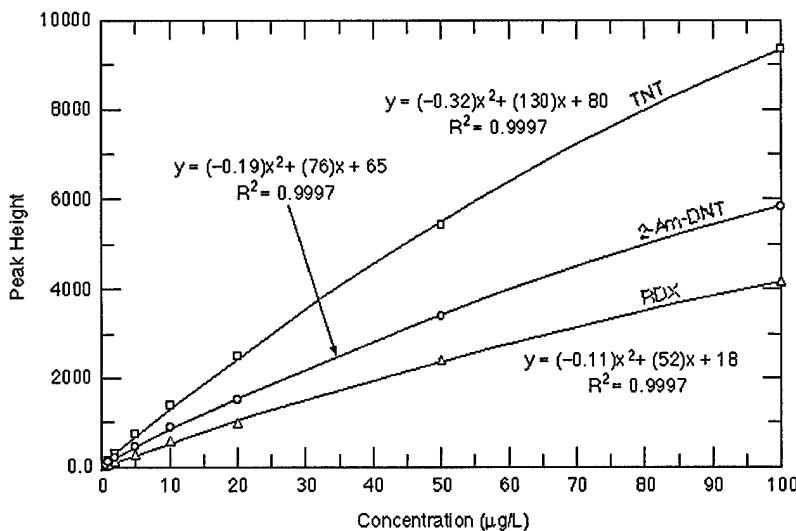
Figure 4. Calibration curves obtained for TNT, 2-Am-DNT, and RDX.

Within the figure:

$y = (-0.32)x^2 + (130)x + 80$
$R^2 = 0.9997$

$y = (-0.19)x^2 + (76)x + 65$
$R^2 = 0.9997$

$y = (-0.11)x^2 + (52)x + 18$
$R^2 = 0.9997$

TNB, TNT, and tetryl were unstable when left at room temperature in amber autosampler vials. Previous stability studies had shown that these analytes were stable for several days in acetonitrile (Jenkins et al. 1988). However, the standards in this previous study were much higher in concentration (3 mg/L). We found that analyte loss was most noticeable at the lower concentrations (50 μg/L vs. 500 μg/L), that the loss differed with different brands of acetonitrile (Table 8), and was slowed by refrigeration of the solution (Fig. 5). The decreases in concentrations of TNB and TNT were confirmed by HPLC to ascertain that the loss was not associated with GC analysis (Table 9). Only the trinitroaromatics exhibited this instability. We were particularly concerned about this instability because samples and standards could

potentially sit in an autosampler for several hours in close proximity to a heated injection port and GC oven vent. The autosampler we used (HP 6890) was designed so that a coolant could be circulated through the tray containing the sample vials. With this modification, the standards were stable over a typical 12-hour analytical shift. The solid-phase extracts of water samples did not exhibit instability, which led us to suspect that residual water from the SPE might stabilize the extracts. However, experiments to establish a link between analyte stability and moisture in the acetonitrile were inconclusive.

Residual water in acetonitrile

Solid-phase extracts will inevitably contain some water. For mid- to nonpolar elution sol-

Table 8. Decrease in peak heights observed for TNB and TNT calibration standards stored at room temperature and prepared with two brands of acetonitrile.

Days at room temp	Baker AcN	Sigma Aldrich AcN	Days at room temp	Baker AcN	Sigma Aldrich AcN
a. Lower concentration			**b. Higher concentration**		
TNB (50 μg/L)			TNB (500 μg/L)		
0	1	1	0	1	1
1	0	0.91	1	0.97	1.00
4	0	0.86	4	0.95	0.97
TNT (50 μg/L)			TNT (500 μg/L)		
0	1	1	0	1	1
1	0.30	0.70	1	0.89	0.93
4	0.20	0.45	4	0.81	0.83
RDX (100 μg/L)			RDX (1000 μg/L)		
0	1	1	0	1	1
1	0.99	1.08	1	1.03	1.06
4	1.16	1.08	4	1.05	1.05

"Peak ht/day 0 peak ht" spanning Baker AcN and Sigma Aldrich AcN columns.

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Table 9. Concentrations (µg/L) of various analytes found by HPLC for standards stored at room temperature in vials in the dark.

Days*	NB	m-NT	DNB	2,6-DNT	2,4-DNT	TNB	TNT	RDX	HMX
Found concentration using HPLC									
Replicate 1									
0	121	554	50.2	54.5	52.7	57.4	52.1	101	489
1	122	566	50.1	54.2	52.2	55.5	37.9	96.7	482
4	123	550	51.9	53.1	53.3	38.9	24.3	106	458
Replicate 2									
0	120	555	50.9	52.7	51.8	57.8	50.5	97.6	479
1	120	548	48.5	50.4	50.6	58.4	44.2	94.0	468
4	121	539	50.8	50.5	52.3	44.7	35.7	103	568
Target concentration									
	119	541	50.6	50.8	51.2	50.4	50.1	100	501

* Time at room temperature.
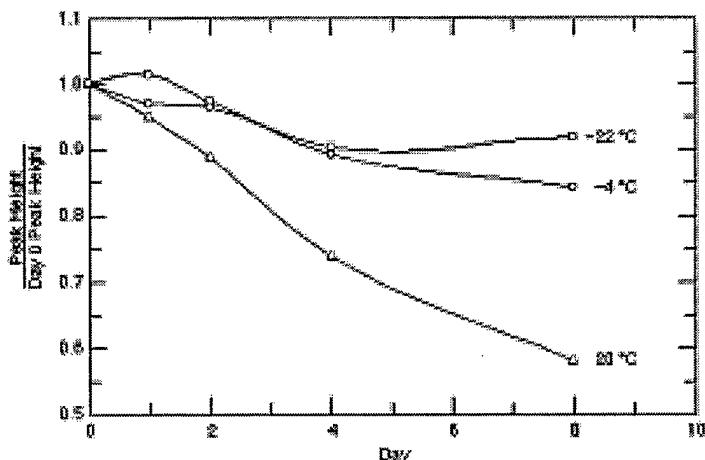
Figure 5. Effect of storage temperature on 10 µg/L TNT calibration standard.

vents, this water is removed from the solvent with anhydrous sodium sulfate. As stated above, we wanted to develop a method in which the sample extract could be analyzed by both GC and by RP-HPLC using Method 8330. Acetonitrile is the most efficient solvent for extraction of the Method 8330 analytes, especially the nitramines. Polar solvents such as acetonitrile are not readily dried.

We prepared acetonitrile solutions with water concentrations of 0 to 20% and analyte concentrations of 25 µg/L DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, 4-Am-DNT, 2-Am-DNT, 50 µg/L RDX, and 250 µg/L HMX (Table 10). Using blocked ANOVA to compare mean peak heights, we found no significant difference between 0%, 10%, 15%, and 20% water. A small difference was observed for 5% water.

We also made a series of standards (2.5 to 30

µg/L) in acetonitrile containing water at a concentration of 10%. We compared the GC response of standards with and without water by linear regression (Fig. 6 shows data for TNT). Slopes ranged from 0.977 to 1.145, bracketing the expected value of 1.00. However, repeated injections of standards containing 10% water resulted in tailing peaks and decreased peak heights of the nitramines and the amino compounds. We suspect that the water degrades the deactivation layer of the injection-port liner. Therefore air-drying of the solid phase prior to elution with acetonitrile is important if the extract is to be analyzed by GC.

Feasibility of SPE and GC-ECD for explosives

Initial spike recovery

SPE has been used to concentrate explosives from water for many years (Jenkins et al. 1992).

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Table 10. Effect of residual water in acetonitrile on peak heights of various analytes.

Analyte	Conc. (μg/L)	Mean peak height (n = 2)				
		0% water	5% water	10% water	15% water	20% water
DNB	25	783	700	718	756	755
2,6-DNT	25	2279	2142	2199	2279	2226
2,4-DNT	25	1458	1339	1408	1436	1427
TNB	25	1023	889	930	962	1038
TNT	25	2125	2001	2073	2149	2202
RDX	50	2963	2684	2740	2808	2695
4-Am-DNT	25	1688	1450	1502	1668	1613
2-Am-DNT	25	1953	1697	1757	1919	1856
HMX	250	9271	7421	9405	10211	9206
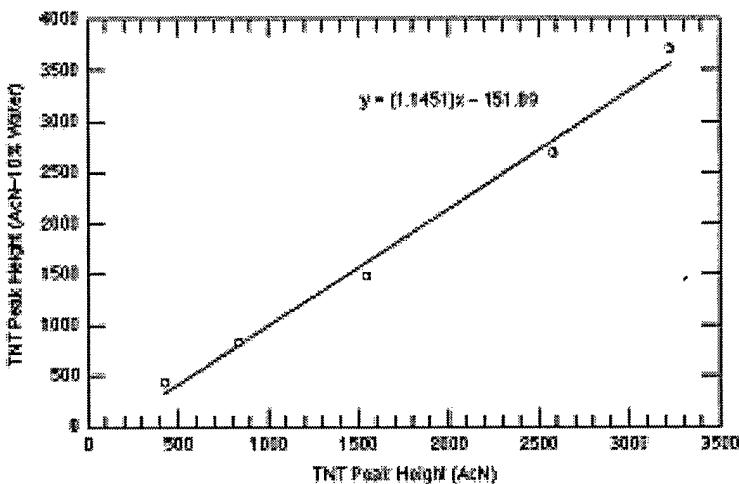
Figure 6. TNT peak heights for acetonitrile solutions containing 10% water vs. solutions without water. Concentrations of TNT were 2.5, 5, 10, 20, and 30 μg/L.

Problems such as low recovery of the nitramines and interfering peaks in HPLC chromatograms have been solved (Jenkins et al. 1995). We performed an initial spike recovery study using the two SPE protocols that are expected to be included in SW-846 Update IV for Method 8330A. These protocols specify preconcentration with Empore SDB-RPS (47-mm-diameter) disks or the Water Sep-Pak Vac Porapak RDX cartridges, and analyte elution with acetonitrile. The purpose of this initial spike recovery was to determine whether a solid-phase extract prepared for analysis by Method 8330 could also be analyzed by GC-ECD.

Using both disks and cartridges, we preconcentrated duplicate 50-mL samples spiked at 5-μg/L aqueous concentration for most of the analytes (Table 11). We divided each 5.0-mL acetonitrile extract and analyzed each by GC-ECD and HPLC-UV. (The portion of acetonitrile extract used for HPLC was mixed 1/1 v/v with water

prior to analysis.) We found good recovery for all the analytes by both methods. In general, repeatability was better using HPLC-UV. Overall, the results indicated that SPE with acetonitrile elution was a feasible sample preparation procedure prior to GC-ECD.

Field samples

We analyzed several solid-phase extracts of water samples collected from various explosives-contaminated sites. These included extracts from LAAP in which 500-mL samples were preconcentrated using Porapak RDX cartridges and eluted with 5 mL acetonitrile. These extracts were prepared and analyzed by HPLC at the U.S. Army Engineer Waterways Experiment Station (Vicksburg, Mississippi). Water samples from Umatilla Army Depot and CFB-Valcartier were preconcentrated at CRREL using either cartridges or Empore disks, with the HPLC analysis performed at

Table 11. Recovery and repeatability of GC and HPLC determinations of analyte concentrations in spiked water samples.

	Spiked conc. (μg/L)	Found conc. (μg/L)		Avg recovery (%)	RPD* (%)
		Membrane 1	Membrane 2		
a. Empore SDB-RPS 47-mm diameter					
GC-ECD					
DNB	5.06	4.77	4.35	90	9.4
2,6-DNT	5.08	4.88	4.48	92	8.7
2,4-DNT	5.12	4.78	4.50	91	6.1
TNB	5.04	4.33	4.25	85	1.7
TNT	5.01	4.72	4.63	93	1.9
RDX	10.0	9.55	9.32	94	2.4
4-Am-2,6-DNT	5.06	4.51	4.28	87	5.1
2-Am-4,6-DNT	5.02	5.74	5.22	109	9.5
HMX	50.1	49.7	47.0	96	5.6
HPLC-UV					
DNB	5.06	5.45	5.26	106	3.7
2,6-DNT and 2,4-DNT†	10.2	10.6	10.2	102	3.9
TNB	5.04	5.62	5.18	107	8.1
TNT	5.01	6.04	5.48	115	9.8
RDX	10.0	10.3	10.3	103	0.2
4-Am-2,6-DNT and 2-Am-4,6-DNT†	10.1	10.8	10.3	105	5.2
HMX	50.1	45.9	46.9	93	2.2

	Spiked conc. (μg/L)	Found conc. (μg/L)		Avg recovery (%)	RPD* (%)
		Cartridge 1	Cartridge 2		
b. Waters Sep-Pak Vac Porapak RDX cartridges					
GC-ECD					
DNB	5.06	5.20	4.66	98	11.1
2,6-DNT	5.08	5.29	4.87	100	8.3
2,4-DNT	5.12	5.03	4.80	96	4.6
TNB	5.04	4.92	4.73	96	3.8
TNT	5.01	5.26	5.07	103	3.7
RDX	10.0	10.8	10.6	106	1.8
4-Am-2,6-DNT	5.06	5.05	4.58	95	9.6
2-Am-4,6-DNT	5.02	5.26	4.85	101	8.1
HMX	50.1	68.8	67.7	136	1.6
HPLC-UV					
DNB	5.06	5.76	5.70	113	1.1
2,6-DNT and 2,4-DNT†	10.16	11.0	11.0	108	0.3
TNB	5.04	5.71	5.67	113	0.7
TNT	5.01	5.97	5.99	119	0.4
RDX	10.0	12.5	12.1	123	3.3
4-Am-2,6-DNT and 2-Am-4,6-DNT†	10.1	10.6	10.6	105	0.4
HMX	50.1	55.5	56.2	111	1.3

* Relative percent difference.
† Peaks not resolved.

CRREL. All GC-ECD analysis was done at CRREL. Gas chromatograms were obtained on the DB–1 analytical column, and RTX-200 and RTX-225 confirmation column (Fig. 7).

All comparisons of HPLC and GC-ECD determinations were done on extract splits. Concentration estimates obtained by the two methods of determination for the most commonly found analytes (HMX, RDX, TNT, TNB, and 2,4-DNT) (Table 12) compared favorably for most samples over a wide range of concentrations. Discrepancies between the two methods of analysis, however, do exist. The GC appeared to underestimate the concentration of RDX in some of the low concentration samples. However, the ECD is a more selective detector, so this apparent underestimation may not be real due to an interference with HPLC. Secondly, tetryl was detected by GC in some LAAP extracts, but not by HPLC. We suspect that when we analyze a tetryl standard by

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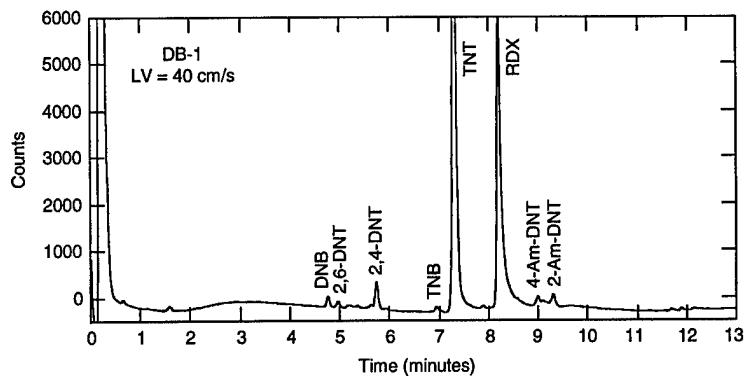
a. DB-1 analytical column.
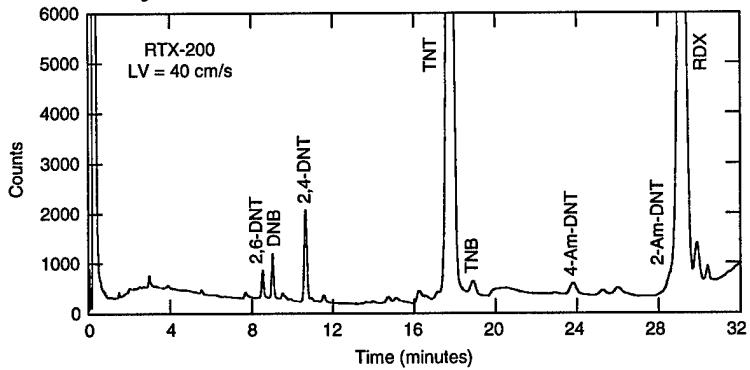
b. RTX-200 confirmation column.
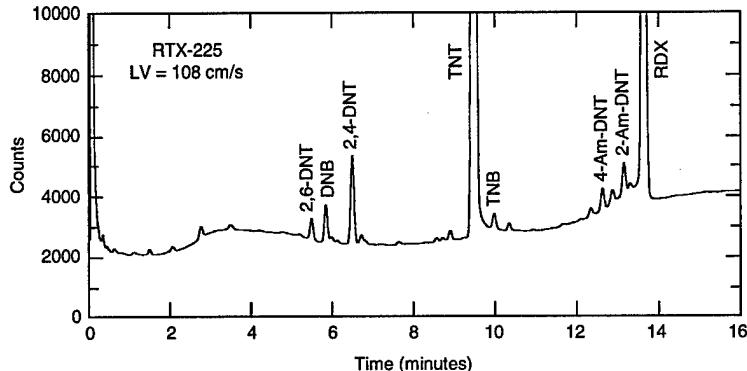
c. RTX-225 confirmation column.

Figure 7. Chromatograms for one water sample obtained from LAAP.

GC the peak we observe actually corresponds to a thermal degradation product of tetryl, possibly n-methyl-picramide (Tamiri and Zitrin 1986). Several LAAP water samples are also contaminated with picric acid, and an unidentified co-contaminant of picric acid is potentially the source of the peak we observe on the GC. Finally, 2,6-DNT was detected by GC-ECD in almost every sample that contained 2,4-DNT. These isomers often coelute on the LC-18 separation specified in Method 8330. However, these isomers can be resolved on other LC columns (Walsh et al. 1993), specifically those with 3-μm phase particles, which are less rugged for routine analysis of large numbers of samples.

Almost all the extracts from field samples re-

quired dilution prior to GC-ECD analysis so that peak heights would fall within the linear calibration range. Dilution actually appeared to improve the accuracy of the GC determination of HMX when several samples were run sequentially. We suspect that dilution served to "clean up" the extracts, diluting residual water and slowing the degradation of the deactivation layer in the injection-port liner and the buildup of non-volatile coextracted contaminants that deposit in the injection-port liner. Accurate determination of HMX required that the injection-port liner be changed frequently. We changed the liner each time we replaced the injection-port septum, at least every 50 injections.

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Table 12. Concentration (µg/L) estimates obtained for the most commonly found analytes by HPLC and GC-ECD for water samples collected at explosives-contaminated sites.

Source	SPE method	Concentration HPLC	Concentration GC-ECD
HMX			
KSS AAP	Cartridge	0.20	0.10
Umatilla	Disk	0.29	0.60
Umatilla	Disk	0.22	0.59
Umatilla	Cartridge	0.31	0.21
LAAP	Cartridge	19	13
CFB-Valcartier	Cartridge	26	26
CFB-Valcartier	Cartridge	97	110
LAAP	Cartridge	116	109
Umatilla	Cartridge	141	179
LAAP	Cartridge	182	147
LAAP	Cartridge	216	217
CFB-Valcartier	Cartridge	219	280
CFB-Valcartier	Cartridge	250	308
CFB-Valcartier	Cartridge	251	285
LAAP	Cartridge	1300	1378
LAAP	Cartridge	1860	1842
RDX			
KSS AAP	Cartridge	0.2	0.2
Umatilla	Disk	0.27	0.20
KSS AAP	Cartridge	1.6	0.95
CFB-Valcartier	Cartridge	1.7	1.0
CFB-Valcartier	Cartridge	2.0	0.56
LAAP	Cartridge	2.4	0.28
LAAP	Cartridge	3.6	0.6
Umatilla	Disk	4.9	4.9
Umatilla	Disk	5.2	5.1
Umatilla	Cartridge	6.5	5.2
Umatilla	Cartridge	6.7	7.0
LAAP	Cartridge	8.9	1.2
CFB-Valcartier	Cartridge	29.8	37.7
CFB-Valcartier	Cartridge	30.9	34.7
CFB-Valcartier	Cartridge	33.8	44.1
LAAP	Cartridge	845	590
LAAP	Cartridge	1430	1973
LAAP	Cartridge	2060	2241
LAAP	Cartridge	3710	3640
LAAP	Cartridge	11800	8175
LAAP	Cartridge	23400	20833

Source	SPE method	Concentration HPLC	Concentration GC-ECD
TNT			
LAAP	Cartridge	0.3	0.5
LAAP	Cartridge	0.4	0.1
LAAP	Cartridge	0.5	0.3
LAAP	Cartridge	2.4	1.2
LAAP	Cartridge	152	142
Umatilla	Cartridge	241	233
LAAP	Cartridge	390	405
LAAP	Cartridge	2430	2876
LAAP	Cartridge	2890	3721
LAAP	Cartridge	7500	7781
LAAP	Cartridge	10500	12168
TNB			
LAAP	Cartridge	0.1	0.02
LAAP	Cartridge	1.0	0.4
LAAP	Cartridge	1.9	1.0
LAAP	Cartridge	15.6	33.8
LAAP	Cartridge	22.3	34.2
LAAP	Cartridge	649	1128
LAAP	Cartridge	742	782
LAAP	Cartridge	9110	11991
LAAP	Cartridge	9150	10640
2,4-DNT*			
LAAP	Cartridge	<d	0.07
LAAP	Cartridge	<d	0.06
LAAP	Cartridge	<d	0.05
LAAP	Cartridge	<d	0.15
LAAP	Cartridge	0.69	0.36
LAAP	Cartridge	10.7	11.8
LAAP	Cartridge	24.5	18.7
LAAP	Cartridge	46.8	33.6
LAAP	Cartridge	127	126
LAAP	Cartridge	142	84.8
LAAP	Cartridge	442	341

* In several extracts, 2,6-DNT was detected by GC-ECD, but not by HPLC.
<d = Less than detection limit.

Spike recovery and method detection limits

To obtain an estimate of the accuracy of the GC method, we spiked seven replicate 500-mL reagent-grade water samples at the concentrations shown in Table 13. The explosives were extracted from the water using Empore SDB-RPS disks, which were eluted with 5.0 mL of acetonitrile, which results in a preconcentration factor of 100. Found concentrations and recoveries were computed using three methods of calibration: average calibration factor, a nonlinear calibration curve, and linear interpolation from the calibration curve.

Concentration estimates (Table 13, Table A1) obtained by the three methods of calibration were similar for many of the analytes. Using average calibration factors for 2,6-DNT, 2,4-DNT, and TNT resulted in estimates that were generally lower than when using a quadratic model or linear interpolation. The calibration factors for each of these analytes, while still within the 20% RSD criteria for linearity, noticeably decline with increasing concentration; estimates of concentrations in real samples will therefore have variable degrees of error depending on the point within the cali-

Table 13. Effect of calibration method on concentration estimates for spiked 500-mL water samples preconcentrated to 5.0 mL acetonitrile using Empore SDB-RPS disks.

Calibration method	Average found concentration (µg/L)																
	DNB	2,6-DNT	2,4-DNT	TNB	TNT	RDX	4-Am-2,6-DNT	2-Am-4,6-DNT	Tetryl	DNA	NB	o-NT	m-NT	p-NT	NG	PETN	HMX
Average cal. factor	0.18	0.16	0.17	0.19	0.18	0.18	0.14	0.16	0.19	0.14	0.95	0.94	0.94	0.91	0.95	1.07	1.74
Nonlinear model	0.20	0.19	0.21	0.19	0.23	0.18	0.15	0.17	0.19	0.15	0.97	0.93	0.92	0.90	0.92	0.99	1.58
Linear interpolation	0.20	0.19	0.21	0.19	0.23	0.18	0.14	0.17	0.19	0.14	0.97	0.92	0.89	0.88	0.90	0.96	1.58
Target conc. (µg/L)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	1.0	1.0	1.0	1.0	1.0	1.0	2.0
	Average recovery (%)																
Average cal. factor	90	82	86	95	91	91	72	79	93	70	95	94	94	91	95	107	87
Nonlinear model	99	93	104	94	116	88	75	87	95	74	97	93	92	90	92	99	79
Linear interpolation	98	93	105	94	116	88	72	87	95	70	97	92	89	88	90	96	79

bration range. Because of the limited linear range of the ECD, a quadratic calibration model appears to yield more accurate concentration estimates than an average calibration factor.

Using estimates based on quadratic calibration models, recovery was 90% or greater for each of the nitroaromatics and nitrate esters. Recoveries were lower for the nitramines and amino-nitrotoluenes, but well within the acceptable range of SW-846 methods. Based on the standard deviations of the means for seven replicates, MDLs were computed (Table 14, Table A2). These MDLs are all below water quality criteria except for 2,6-DNT 10^{-6} for increased cancer risk.

We obtained a lower MDL for 2,6-DNT (0.0025 µg/L) by extracting a greater volume of water (1 L), eluting with less acetonitrile (4.0 mL), spiking at lower concentrations (Grant et al. 1991), and using 10 replicates. We used both cartridge and disk SPE (Table 15, Table A2), and the MDLs were generally quite similar for each analyte. If the analyte of most interest is 2,6-DNT, the MDL could be lowered even more by preconcentrating a greater volume of water. We limited the volume we preconcentrated to prevent breakthrough of HMX and RDX. 2,6-DNT is well retained on both solid

Table 14. Recovery data and MDLs for various analytes for 500-mL water samples preconcentrated to 5.0 mL acetonitrile using Empore SDB-RPS disks.

Analyte	Mean* found conc. (µg/L)	Target conc. (µg/L)	Mean recovery (%)	RSD (%)	MDL (µg/L)
DNB	0.197	0.20	99	9.7	0.06
2,6-DNT	0.187	0.20	93	7.1	0.04
2,4-DNT	0.208	0.20	104	7.6	0.05
TNB	0.189	0.20	94	7.7	0.05
TNT	0.233	0.20	116	8.0	0.06
RDX	0.176	0.20	88	7.2	0.04
4-Am-2,6-DNT	0.150	0.20	75	11.2	0.05
2-Am-4,6-DNT	0.174	0.20	87	11.6	0.06
Tetryl	0.190	0.20	95	8.3	0.05
DNA	0.148	0.20	74	9.2	0.04
NB	0.969	1.0	97	7.1	0.2
o-NT	0.927	1.0	93	5.1	0.2
m-NT	0.918	1.0	92	4.6	0.1
p-NT	0.897	1.0	90	5.3	0.2
NG	0.918	1.0	92	5.5	0.2
PETN	0.992	1.0	99	4.8	0.2
HMX	1.58	2.0	79	8.1	0.4

* Mean of seven replicate 500-mL water samples preconcentrated to 5 mL AcN using Empore SDB-RPS disks. Complete data set is in Table A1.

Table 15. MDLs (μg/L) for some target analytes when 1-L water samples were preconcentrated to 4.0 mL acetonitrile using cartridge and disk solid-phase extraction.

	Spiked conc. (μg/L)	MDLs* by GC-ECD Cartridge	MDLs* by GC-ECD Disk
DNB	0.01	0.004	0.003
2,6-DNT	0.01	0.003	0.003
2,4-DNT	0.01	0.009	0.01
TNB	0.01	0.007	0.003
TNT	0.01	0.01	0.02[†]
RDX	0.01	0.004	0.02[†]
4-Am-2,6-DNT	0.01	0.003	0.003
2-Am-4,6-DNT	0.01	0.003	0.004
Tetryl	0.01	0.009	0.01
HMX	0.01	0.004	0.008

* Data in Table A2.
† MDLs are greater than spiked concentration and therefore are not valid.

phases, and the volume of water preconcentrated is more likely limited by practical considerations such as time or possible plugging of the solid phase.

CONCLUSIONS

A gas chromatographic method for the determination of explosives in water was developed to serve as an alternative to and/or complement the current HPLC SW-846 Method 8330. Water samples are preconcentrated using SPE, and the acetonitrile extracts are directly injected onto a short (6 m) DB-1 analytical column. High linear carrier gas velocities resulted in higher peak heights for the nitramines and nitrate esters, the most thermally labile analytes. MDLs ranged from 0.04 to 0.4 μg/L when 0.5 L of water samples was preconcentrated to 5.0 mL acetonitrile. Lower MDLs for some analytes, such as 2,6-DNT, were obtained by preconcentrating a larger volume of water.

Analysis of extracts from field samples showed good agreement between the GC-ECD and the standard HPLC method.

Potential advantages over the current HPLC method include lower detection limits, improved chromatographic resolution, and the utilization of instrumentation most commonly found in environmental labs. Disadvantages of the GC method include nonlinear calibration, limited dynamic range of the detector, and increased attention to instrument maintenance (i.e., frequent changes of the injection-port liner). Also, the low concentration calibration standards used for GC require refrigeration to maintain analyte stability.

Combined use of GC-ECD and HPLC will provide an improved method for analyte confirmation because chromatographic separations are based on different physical properties (vapor pressure and polarity) and the detectors are based on different principles (electronegativity and UV absorption).

This method is under review by the EPA Office of Solid Waste as SW-846 Method 8095: Explosives in Water by Gas Chromatography.

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APPENDIX A: DATA

Table A1. Concentration (µg/L) estimates obtained using three different calibration methods for seven replicate spiked samples.

Rep	Average CF*	Quadratic	Interpolation	Rep	Average CF*	Quadratic	Interpolation
Nitroaromatics: spiked concentration 0.2 µg/L				**Nitroaromatics: spiked concentration 1 µg/L**			
DNB				**NB**			
1	0.166	0.170	0.166	1	0.91	0.92	0.92
2	0.190	0.213	0.214	2	0.94	0.96	0.95
3	0.187	0.209	0.210	3	1.05	1.09	1.08
4	0.160	0.169	0.167	4	0.89	0.90	0.90
5	0.184	0.200	0.200	5	0.91	0.92	0.92
6	0.183	0.209	0.211	6	1.01	1.04	1.03
7	0.189	0.210	0.210	7	0.95	0.97	0.97
Mean	0.180	0.197	0.197	Mean	0.95	0.97	0.97
Recovery (%)	90	99	98	Recovery (%)	95	97	97
2,6-DNT				**o-NT**			
1	0.158	0.169	0.166	1	0.89	0.88	0.87
2	0.172	0.199	0.200	2	0.90	0.89	0.88
3	0.170	0.197	0.198	3	0.95	0.95	0.94
4	0.152	0.169	0.169	4	0.91	0.90	0.89
5	0.165	0.184	0.183	5	0.92	0.92	0.91
6	0.162	0.189	0.190	6	1.02	1.02	1.01
7	0.173	0.200	0.201	7	0.95	0.94	0.93
Mean	0.165	0.187	0.187	Mean	0.94	0.93	0.92
Recovery (%)	82	93	93	Recovery (%)	94	93	92
2,4-DNT				**m-NT**			
1	0.159	0.175	0.175	1	0.90	0.87	0.85
2	0.176	0.213	0.215	2	0.92	0.90	0.87
3	0.178	0.220	0.222	3	0.95	0.94	0.91
4	0.168	0.206	0.208	4	0.91	0.88	0.86
5	0.177	0.212	0.214	5	0.92	0.90	0.88
6	0.174	0.222	0.223	6	1.01	1.00	0.97
7	0.173	0.205	0.207	7	0.95	0.93	0.90
Mean	0.172	0.208	0.209	Mean	0.94	0.92	0.89
Recovery (%)	86	104	105	Recovery (%)	94	92	89
TNB				**p-NT**			
1	0.177	0.169	0.166	1	0.85	0.83	0.81
2	0.197	0.197	0.198	2	0.91	0.90	0.87
3	0.203	0.206	0.208	3	0.92	0.91	0.89
4	0.175	0.170	0.170	4	0.89	0.87	0.85
5	0.191	0.187	0.186	5	0.90	0.89	0.87
6	0.190	0.192	0.193	6	1.00	0.99	0.97
7	0.200	0.200	0.200	7	0.92	0.90	0.88
Mean	0.190	0.189	0.189	Mean	0.91	0.90	0.88
Recovery (%)	95	94	94	Recovery (%)	91	90	88
TNT							
1	0.178	0.210	0.214				
2	0.186	0.241	0.241				
3	0.189	0.255	0.250				
4	0.169	0.209	0.211				
5	0.182	0.223	0.226				
6	0.180	0.248	0.241				
7	0.188	0.243	0.243				
Mean	0.182	0.233	0.232				
Recovery (%)	91	116	116				

* Calibration factor

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Table A1 (cont'd). Concentration (μg/L) estimates obtained using three different calibration methods for seven replicate spiked samples.

Rep	Average CF*	Quadratic	Interpolation
Amino-nitrotoluenes: spiked concentration 0.2 (μg/L)			
4-Am-2,6-DNT			
1	0.136	0.136	0.126
2	0.154	0.165	0.161
3	0.157	0.171	0.168
4	0.125	0.125	0.117
5	0.138	0.139	0.131
6	0.148	0.162	0.159
7	0.146	0.152	0.145
Mean	0.143	0.150	0.144
Recovery (%)	72	75	72
2-Am-4,6-DNT			
1	0.148	0.150	0.142
2	0.165	0.184	0.187
3	0.171	0.204	0.210
4	0.141	0.148	0.144
5	0.157	0.167	0.165
6	0.159	0.185	0.189
7	0.163	0.180	0.180
Mean	0.158	0.174	0.174
Recovery (%)	79	87	87
Dinitroaniline			
1	0.134	0.140	0.135
2	0.141	0.148	0.142
3	0.160	0.171	0.163
4	0.137	0.144	0.138
5	0.139	0.146	0.140
6	0.151	0.160	0.153
7	0.125	0.129	0.125
Mean	0.141	0.148	0.142
Recovery (%)	70	74	71
Nitramines: spiked concentration 0.2 μg/L			
RDX			
1	0.159	0.151	0.151
2	0.177	0.170	0.170
3	0.184	0.179	0.178
4	0.187	0.183	0.182
5	0.194	0.189	0.188
6	0.187	0.183	0.182
7	0.181	0.174	0.174
Mean	0.181	0.176	0.175
Recovery (%)	91	88	88
Tetryl			
1	0.169	0.170	0.168
2	0.193	0.198	0.198
3	0.201	0.207	0.207
4	0.165	0.167	0.166
5	0.187	0.190	0.189
6	0.194	0.201	0.201
7	0.194	0.199	0.198
Mean	0.186	0.190	0.189
Recovery (%)	93	95	95

Rep	Average CF*	Quadratic	Interpolation
Nitramines: spiked concentration 2 μg/L			
HMX			
1	1.61	1.47	1.48
2	1.88	1.70	1.70
3	1.98	1.79	1.78
4	1.61	1.47	1.47
5	1.77	1.61	1.61
6	1.62	1.48	1.48
7	1.69	1.54	1.55
Mean	1.74	1.58	1.58
Recovery (%)	87	79	79
Nitrate esters: spiked concentration 1.0 μg/L			
NG			
1	0.89	0.85	0.83
2	0.93	0.89	0.87
3	0.97	0.94	0.92
4	0.92	0.88	0.86
5	0.97	0.93	0.91
6	1.03	1.00	0.98
7	0.97	0.94	0.92
Mean	0.95	0.92	0.90
Recovery (%)	95	92	90
PETN			
1	1.01	0.93	0.90
2	1.03	0.95	0.92
3	1.05	0.97	0.94
4	1.09	1.01	0.98
5	1.11	1.03	1.00
6	1.16	1.07	1.05
7	1.06	0.98	0.94
Mean	1.07	0.99	0.96
Recovery (%)	107	99	96

*Calibration factor

Table A2. MDLs obtained when 10 replicate 0.01 µg/L 1-L water samples were preconcentrated to 4.0 mL acetonitrile using either cartridge or disk SPE.

Rep	DNB	2,6-DNT	2,4-DNT	TNB	TNT	RDX	4-Am-2,6-DNT	2-Am-4,6-DNT	Tetryl	HMX
Waters Porapak RDX Sep-Pak Vac										
1	0.0080	0.0052	0.0090	0.0096	0.0131	0.0101	0.0066	0.0120	0.0039	0.0082
2	0.0085	0.0064	0.0078	0.0109	0.0184	0.0064	0.0069	0.0093	0.0100	0.0066
3	0.0099	0.0073	0.0098	0.0131	0.0091	0.0071	0.0079	0.0090	0.0106	0.0102
4	0.0107	0.0081	0.0126	0.0136	0.0245	0.0072	0.0089	0.0102	0.0123	0.0086
5	0.0090	0.0077	0.0102	0.0090	0.0149	0.0067	0.0084	0.0092	0.0123	0.0068
6	0.0120	0.0086	0.0186	0.0146	0.0180	0.0084	0.0092	0.0115	0.0127	0.0098
7	0.0100	0.0077	0.0115	0.0138	0.0236	0.0067	0.0080	0.0094	0.0102	0.0072
8	0.0083	0.0078	0.0100	0.0087	0.0205	0.0107	0.0087	0.0097	0.0117	0.0068
9	0.0099	0.0076	0.0104	0.0128	0.0115	0.0063	0.0082	0.0091	0.0126	0.0072
10	0.0110	0.0085	0.0154	0.0148	0.0201	0.0073	0.0092	0.0095	0.0173	0.0102
Mean	0.0097	0.0075	0.0115	0.0121	0.0174	0.0077	0.0082	0.0099	0.0114	0.0082
Std. dev.	0.0013	0.0010	0.0032	0.0023	0.0051	0.0016	0.0009	0.0011	0.0033	0.0015
MDL	0.0036	0.0029	0.0092	0.0066	0.0144	0.0044	0.0026	0.0030	0.0094	0.0041
Recovery (%)	97	75	115	121	174	77	82	99	114	82
Empore SDB-RPS										
1	0.0101	0.0092	0.0197	0.0079	0.0305	0.0255	0.0104	0.0131	0.0148	0.0115
2	0.0076	0.0068	0.0167	0.0069	0.0171	0.0075	0.0078	0.0091	0.0120	0.0070
3	0.0088	0.0087	0.0136	0.0070	0.0167	0.0075	0.0088	0.0100	0.0198	0.0113
4	0.0077	0.0074	0.0117	0.0064	0.0115	0.0068	0.0083	0.0091	0.0136	0.0067
5	0.0080	0.0078	0.0118	0.0060	0.0127	0.0061	0.0080	0.0089	0.0146	0.0074
6	0.0079	0.0077	0.0119	0.0063	0.0104	0.0066	0.0084	0.0093	0.0123	0.0043
7	0.0083	0.0073	0.0100	0.0055	0.0089	0.0056	0.0078	0.0090	0.0108	0.0043
8	0.0075	0.0073	0.0086	0.0059	0.0105	0.0054	0.0078	0.0089	0.0107	0.0046
9	0.0072	0.0065	0.0078	0.0050	0.0073	0.0050	0.0067	0.0075	0.0075	0.0036
10	0.0071	0.0065	0.0088	0.0049	0.0071	0.0052	0.0068	0.0076	0.0084	0.0045
Mean	0.0080	0.0075	0.0121	0.0062	0.0133	0.0081	0.0081	0.0092	0.0124	0.0065
Std. dev.	0.0009	0.0009	0.0038	0.0009	0.0070	0.0062	0.00105	0.0016	0.0035	0.0029
MDL	0.0025	0.0025	0.0106	0.0027	0.0196	0.0174	0.0030	0.0044	0.0100	0.0081
Recovery (%)	80	75	121	62	133	81	81	92	124	65

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APPENDIX B: DETERMINATION OF NITROAROMATICS, NITRAMINES, AND NITRATE ESTERS BY SPE AND GC-ECD

1.0 SCOPE AND APPLICATION

This method is intended for the trace analysis of explosives residues in water; it provides gas chromatographic (GC) conditions for the detection of the ppb levels using an electron capture detector (ECD). All of these compounds are used as explosives, are by-products of the manufacture of explosives, or are the transformation products of explosives. This method is restricted to use by or under the supervision of analysts experienced in the use of GC-ECD, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. Also, each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method provides two optional procedures for preconcentration of low concentration (parts per trillion, or nanograms per liter) of certain explosives residues in surface or groundwater. These options are cartridge solid-phase extraction and disk solid-phase extraction.

2.1 Cartridge solid-phase extraction

For each sample, a Waters Sep-Pak Vac Porapak RDX cartridge is placed on a solid-phase extraction vacuum manifold. The solid phase is conditioned by passing acetonitrile through each cartridge. Then reagent-grade water is pulled through each cartridge to rinse away the acetonitrile. Next, the analytes are extracted by pulling the aqueous samples through cartridges at low flow rate. Air is then pulled through each cartridge to remove excess water. Finally, the cartridges are eluted using acetonitrile.

2.2 Disk solid-phase extraction

For each sample, an Empore styrene-divinyl benzene reverse-phase sulfonated resin (SDB-RPS) disk is placed on a vacuum filter apparatus and preconditioned with acetonitrile. The acetonitrile is pulled through each disk, followed by reagent-grade water, and then the water sample. Air is then pulled through each disk to remove excess water. Finally, the disks are eluted using acetonitrile.

2.3 GC-ECD determinations

Acetonitrile extracts are directly injected into the heated inlet of a gas chromatograph equipped with an electron capture detector. The analytes are resolved on a wide-bore fused-silica capillary column coated with polydimethylsiloxane.

3.0 DEFINITIONS

Compound	Abbreviation	CAS* number
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	TNB	99-35-4
1,3-Dinitrobenzene	DNB	99-65-0
2,4,6-trinitrophenylmethyl-nitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4,6-dinitrotoluene	2-Am-DNT	35572-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0
3,5-Dinitroaniline	3,5-DNA	618-87-1
Nitroglycerine	NG	55-63-0
Pentaerythritoltetranitrate	PETN	78-11-5

*Chemical Abstract Service Registry Number

4.0 INTERFERENCES

4.1 Sample processing hardware

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interference.

4.2 Detector

In addition to nitrogenated organics, the ECD will respond to other electrophores such as halogenated and oxygenated compounds. No specific compounds have been identified as interferences.

4.3 Injector

The injection-port liner must be deactivated to

prevent adsorption of several of the analytes. After several injections of sample extracts, deposition of nonvolatile residues may result in peak tailing and a decline in the response for HMX. The injection-port liner must be changed or cleaned each time the septum is replaced, at least every 50 injections.

5.0 SAFETY

Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by this method. The only extra precaution that should be taken is when handling the analytical standard neat material of the explosives. Follow the note for drying the neat materials at ambient temperatures in Step 10.1.

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation, GC system
1. GC equipped with the following:
   a. Heated injection port for 0.53-mm-i.d. capillary columns.
   b. Deactivated direct injection liners (Restek #20964 or equivalent).
   c. ECD detector (Ni^{63}).
   d. Temperature-programmable oven.
2. Recommended primary column: Fused-silica 100% polydimethylsiloxane, 0.53-mm i.d., 1.5 μm, 6 m (DB-1 or equivalent).
3. Recommended secondary columns:
   a. Fused-silica trifluoropropyl methylpolysiloxane, 0.53-mm i.d., 1.5 μm, 6 m (Restek RTX-200 or equivalent).
   b. Fused-silica RTX-225 (50% cyanopropylmethyl–50% phenyl methylpolysiloxane) 0.53-mm i.d., 1 μm, 6 m.
4. Data system for peak integration (HP 3365 ChemStation or equivalent).
5. Hydrogen for carrier gas (99.99999+% purity), from cylinder or generator (Whatman Model 75-32 or equivalent).
6. Nitrogen for makeup gas (99.9995% purity, oxygen- and moisture-free), from cylinder or generator (Whatman 75-92 or equivalent).
7. Autosampler with ability to refrigerate vials (HP 6890 or equivalent) (optional).

6.2 Instrumentation, other
1. Balance plus-minus 0.0001 g.
2. Refrigerated circulating bath (Neslab Endocal or equivalent).

6.3 Labware
1. Microliter syringes if making manual injections (Hamilton series 701 liquid syringe, or equivalent).
2. Disposable cartridge filters: 0.45 micron (Millex SR or equivalent).
3. Pipets: Class A, glass, appropriate sizes.
4. Pasteur pipets.
5. Autosampler vials.
6. Disposable syringes: Plastipak, 3 mL (or equivalent).
7. Volumetric flasks: appropriate sizes, with ground-glass stoppers, Class A.
8. Vacuum desiccator: glass.
9. Graduated cylinders: 5.00 mL.

6.4 Equipment specific to cartridge SPE
1. Visiprep Solid-Phase Extraction Manifold: (Supelco 5-7030 or equivalent).
2. Visiprep large volume sampler (Supelco #5-7275).
3. Porapak RDX (divinylbenzene/vinylpyrrolidone) Sep-Pak Vac Cartridges (one per sample) (Waters # WATO47220).

6.5 Equipment specific to disk SPE
1. Vacuum filter apparatus, glass: 47 mm, with manifold or 1-L vacuum flask.
2. Empore SDB-RPS disks: 47-mm (one per sample) (Empore #1214-5026).

7.0 REAGENTS AND STANDARDS

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination or causing interferences.

- Acetonitrile (CH_3CN), for HPLC, GC, pesticide residue analysis, spectrophotometry.

- Acetone (CH_3COCH_3), for HPLC, GC, pesticide residue analysis, spectrophotometry.

- Isopropanol ($[CH_3]_2CHOH$), for HPLC, GC, pesticide residue analysis, spectrophotometry.

- Methanol (CH_3OH) for HPLC, GC, pesticide residue analysis, spectrophotometry.

- SARMs (Standard Analytical Reference Mate-

rial) for each analyte obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. (Calibration standards are commercially available from several sources including Supelco, Accu Standard, Radian.)

8.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

8.1 Sample collection

Follow conventional sampling and sample handling procedures as specified for semivolatile organics in SW-846, Chapter 4.

8.2 Preservation and holding times

Water samples must be stored in the dark at 4°C. Acetonitrile extracts should be stored in the freezer. Holding times are the same as for semivolatile organics.

9.0 QUALITY CONTROL

Refer to SW-846, Chapter 1, for specific quality control procedures.

9.1 Sample extraction validation

Refer to Method 3500.

9.2 GC system validation

Refer to SW-846, Method 8000, Section 8.

9.3 Predetermination of interferences

Prior to preparation of stock solutions, the acetonitrile should be analyzed to determine possible interferences with analyte peaks. If the acetonitrile shows any contamination, a different batch or lot should be used.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Preparation of stock standards solutions

10.1.1

Dry about 0.15 g of each solid analyte standard (SARM) to a constant weight in a vacuum desiccator in the dark.

Note: The HMX, RDX, tetryl, PETN, and 2,4,6-TNT are explosives and the neat material should be handled carefully. HMX, RDX, and tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. Do NOT dry at heated temperatures.

Note: NG is a liquid and should not be dried.

10.1.2

Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100-mL flask and fill to volume with acetonitrile. The NG SARM is a solution of NG in acetone, which should be diluted with acetonitrile.

10.1.3

Invert the flask several times until the analyte is dissolved. Store this stock solution in a refrigerator at 4°C in the dark. Stock solutions may be used for up to one year.

10.1.4

Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1000 mg/L).

10.2 Preparation of intermediate standards solutions

10.2.1

Prepare two intermediate standard solutions by combining appropriate volumes of the various stock solutions. The ECD response is dependent on the number of nitro groups. Response is greatest for TNT and least for the nitrotoluenes. One (A) intermediate stock solution should contain DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, RDX, 4-Am-DNT, 2-Am-DNT, tetryl, and HMX at 1000 μg/L; the second (B) solution should contain NB, o-NT, m-NT, p-NT, NG, and PETN at 5000 μg/L and DNA at 1000 μg/L. These solutions should be stored in a freezer.

10.2.2

Prepare working standard solutions covering the range of interest. Suggested ranges are within 0.5 to 500 μg/L for one (A) set, and 2.5 to 2500 μg/L for the other (B) set; prepare by diluting the two concentrated intermediate stock solutions with acetonitrile. These solutions should be stored in a freezer, and may be used for 30 days. At a minimum, a five-point calibration curve is generated.

Note: The analytes TNB, TNT, and tetryl are unstable at low concentrations in some brands of acetonitrile. If the response for these analytes declines with time, another brand of acetonitrile should be used. All standards should be kept refrigerated at all times.

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10.3 Preparation of surrogate spiking solution

The analyst should monitor the performance of the extraction and analytical system, as well as the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and reagent water blank with one or two surrogates (i.e., analytes not expected to be in the sample but having properties similar to the target analytes). Suggested surrogates are 2,5-DNT or 3,4-DNT spiked at an aqueous concentration of 0.2 µg/L. Each laboratory should generate control limits and should expect recoveries of 70 to 125%.

10.4 Preparation of matrix spiking solutions

Prepare matrix spiking solutions in acetonitrile such that the concentration in the sample is 0.2 µg/L for DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, RDX, 4-Am-DNT, 2-Am-DNT, tetryl, and DNA, 1.0 µg/L for NB, o-NT, m-NT, p-NT, NG, and PETN, and 2.0 µg/L for HMX. All target analytes should be included. Because RDX and PETN coelute on the DB-1 column, these analytes should be in separate spiking solutions.

10.5 Preparation of materials

Prepare all materials to be used as described in SW-846, Chapter 4, for semi-volatile organics.

10.6 Calibration of GC

10.6.1

The GC column should be baked at the injection-port temperature until the baseline is stable. (The injection-port temperature should not be set higher than the maximum column temperature recommended by the column manufacturer.)

10.6.2

The GC conditions for the analytical column are as follows:

GC: HP 5890 with electron capture detector (Ni^{63}).

Analytical column: 6-m- × 0.53-mm-i.d. fused-silica polydimethylsiloxane (J and W DB-1 or equivalent), 1.5- or 3.0-µm film thickness.

Injection-port liner: Restek Direct Injection Uniliner (deactivated).

Injection-port temperature: 250°C.

Injection volume: 1 µL.

Carrier: Hydrogen (linear velocity 40 to 125 cm/s).

Note: Peak resolution is greatest at low linear velocity, but GC response for some analytes is greatest at high linear velocity. The linear velocity should be chosen based on the objectives of the analysis. A mid-range linear velocity of about 80 cm/s will be suitable for most analysis.

Makeup: Nitrogen (38 mL/min)

Oven program 100°C for 2 min, 10°C per min ramp to 200°C, 20°C/min ramp to 250°C, 5 min hold.

Detector temperature: 300°C

GC conditions for the confirmation columns are as follows:
RTX-200
    a. Linear velocity 40 cm/s. Oven 100°C for 1.2 min, 5°C/min to 140°C, 1°C/min to 160°C, 20°C/min to 250°C, hold. Injector 250°C. Detector 290°C.
    b. Linear velocity 122 cm/s (for confirmation of HMX). Oven 150°C for 1 min, 20°C/min to 250°C, hold. Injector 270°C. Detector 290°C.
RTX-225
Linear velocity 108 cm/s. Oven 100°C for 2 min, 10°C/min to 220°C, hold for 8 min. Injector 220°C (column maximum). Detector 250°C.

10.6.3

For initial calibration, injections of each calibration standard over the concentration range of interest are made sequentially into the GC. Peak heights are obtained for each analyte. Because of the limited linear range of the ECD, a linear calibration curve that passes through the origin is not appropriate for each analyte over the entire concentration range listed above. A linear calibration that passes through the origin may be appropriate for the five lowest standards. Alternatively, a nonlinear calibration model may be used as described in SW-846, Chapter 4, Method 8000B.

10.6.4

For daily calibration, analyze the midpoint calibration standards from sets A and B, at a minimum, at the beginning of the day, after every 10 samples, and after the last sample of the day. Obtain the calibration factor for each analyte from the peak heights, and compare it with the response factor obtained for the initial calibration. The calibration factor for the daily calibration must agree within ±15% of the calibration factor of the initial calibration. If this criterion is not met, calculate the average of the responses for all analytes as described in SW-846, Chapter 4,

Method 8000B. If the average exceeds ±15% of the average from the initial calibration, a new initial calibration must be obtained.

11.0 PROCEDURE

11.1 Method number 1: Cartridge solid-phase extraction

11.1.1

For each sample, place an unused Waters Sep-Pak Vac Porapak RDX cartridge on a solid-phase extraction manifold and clean and condition the solid phase by eluting with 30 mL of acetonitrile by gravity flow, followed by 50 mL of reagent-grade water at 10 mL per minute. Air must NOT pass through the cartridge between the acetonitrile and the reagent water. (Note: if air passes through the cartridge, recondition the cartridge with acetonitrile followed by water.) Just before the last of the reagent water is pulled through, turn off the vacuum.

11.1.2

Measure up to a 1000-mL aliquot of each water sample using a 1-L graduated cylinder or volumetric flask. (Alternatively, mark the level of sample on the sample bottle, then measure the sample volume by measuring the volume of water required to refill the bottle after the sample is removed.) Pull the samples through the cartridges at about 10 mL per minute by turning on and adjusting the vacuum.

11.1.3

Once all the sample has been drawn through a cartridge, draw air through the cartridge for *15 minutes* in order to remove any excess water. Turn the vacuum off. *Remove any drops of water that may be clinging to the cartridge tip.*

11.1.4

Elute the samples by passing a 4-mL aliquot of acetonitrile through each cartridge at about 1 mL per minute (gravity flow) and collect the extract in a 5-mL graduated cylinder. Measure the actual volume (±0.1 mL) of the solvent extract.

11.1.5

If the extract is turbid, filter through a Millex-SR filter unit.

11.1.6

Store extracts in a freezer until analysis.

11.2 Method number 2: Disk solid-phase extraction

11.2.1

For each sample, place an Empore SDB-RPS disk on the center of a 47-mm vacuum filter apparatus and moisten with acetone so that the disk adheres to the filter base. Assemble the reservoir and ascertain that the disk is centered so that the water sample will pass through the disk, not around an edge.

11.2.2

To condition each disk, follow manufacturer's directions for rinses with 10 mL each of acetone, isopropanol, and methanol. For the final organic solvent rinse, add a 20-mL aliquot of acetonitrile and allow the acetonitrile to soak into the disks for three minutes. Turn on the vacuum and allow most (but not all) of the acetonitrile to be pulled through the disk. Repeat with a second 20-mL aliquot of acetonitrile.

11.2.3

Add a 50-mL aliquot of reagent-grade water to the reservoir and turn the vacuum on once again, pulling the water through the disk. Just before the last of the water is pulled through, repeat with a second 50-mL aliquot of reagent-grade water. Just before the last of the water is pulled through, turn the vacuum off. The disk must not be allowed to dry between the acetonitrile and water rinses. If air is accidentally pulled through the disk, recondition the disk with acetonitrile (11.2.2).

11.2.4

Fill the reservoir with a 250-mL aliquot of water sample, turn the vacuum on, and begin to pull the sample through the disk. Refill the reservoir as needed. (Alternatively, a 1-L bottle may be inverted onto the reservoir, and the sample will flow from the bottle without overflowing the reservoir.) A 1-L sample should take less than 15 minutes, with resulting flow rates ranging from 70 to 100 mL per minute.

11.2.5

Once all the sample has been drawn through the disk, draw air through the disk for *20 minutes* in order to remove any excess water. Turn the vacuum off. *Remove any drops of water that may be clinging to the tip of the funnel base.*

11.2.6

Place a test tube in the vacuum flask or manifold such that it fits over the funnel exit when the flask or manifold is reattached to the fritted base. The actual size of the test tube depends upon the brand of vacuum flask or manifold.

11.2.7

Add a 5-mL aliquot of acetonitrile to the reservoir, and allow this acetonitrile to soak into the disk for three minutes. Apply the vacuum, drawing the acetonitrile through the disk into the test tube. Use a Pasteur pipet to transfer the solvent extract to a 5-mL graduated cylinder, and measure the actual volume (±0.1 mL) of the solvent extract.

11.2.8

If the extract is turbid, filter through a Millex-SR filter unit.

11.2.9

Store extracts in a freezer until analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

Analyze the samples using the chromatographic conditions given for the GC in Section 10.8.

Follow Section 7 in SW-846, Method 8000B, for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

13.0 POLLUTION PREVENTION

All containers of organic solvents and extraction solutions should be kept capped to prevent evaporation. A large tray should be used under the work area to contain any spilled solvents.

14.0 WASTE MANAGEMENT

All waste should be disposed of according to federal, state, and local regulations.

15.0 REFERENCES

Hable, M., C. Stern, C. Asowata, and K. Williams (1991) The determination of nitroaromatics and nitramines in ground and drinking water by wide-bore capillary gas chromatography. *Journal of Chromatographic Science*, 29: 131–135.

USEPA (1996) Test method for evaluating solid waste: Physical/chemical methods (SW-846). U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C.

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An analytical method for the determination of nitroaromatic, nitramine, and nitrate ester explosives and co-contaminants in water was developed based on SPE (solid-phase extraction) and GC-ECD (gas chromatograph-electron capture detector). Water samples are preconcentrated using either cartridge or membrane SPE followed by elution with acetonitrile. The acetonitrile extract is compatible with both liquid and gas chromatography, thereby allowing direct comparison of concentration estimates obtained by different methods of determination. Quantitative GC analyses were obtained by using deactivated direct-injection-port liners, short wide-bore capillary columns, and high linear carrier gas velocities. Recoveries from spiked samples were 90% or greater for each of the nitroaromatics and nitrate esters, and greater than 70% for nitramines and amino-nitrotoluenes. Estimates of analyte concentrations in well-water extracts from military sites in the United States and Canada analyzed by GC-ECD and the standard HPLC (high performance liquid chromatography) method showed good agreement for the analytes most frequently detected (HMX [octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine], RDX [hexahydro-1,3,5-trinitro-1,3,5-triazine], TNT [2,4,6-trinitrotoluene], and TNB [1,3,5-trinitrobenzene]). The GC method provides lower method detection limits for most analytes than HPLC, but accurate calibration is more difficult. The ultraviolet (UV) detector used for the HPLC analysis has much greater linear range than the ECD

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used for GC analysis. In addition, the GC instrumentation requires more care than the LC. Specifically, the injection port liner must be changed frequently to maintain accurate determination of the nitramines. Because the sample preparation technique yields extracts that are compatible with both GC and HPLC analysis, confirmation of analyte presence can be obtained based on different physical properties.

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